

# Emissions of Trace Products of Incomplete Combustion from a Pilot-Scale Incinerator Secondary Combustion Chamber

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## ABSTRACT

Experiments were performed on a 73 kW rotary kiln incinerator simulator equipped with a 73 kW secondary combustion chamber (SCC) to examine emissions of products of incomplete combustion (PICs) resulting from incineration of carbon tetrachloride ( $\text{CCl}_4$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). Species were measured using an on-line gas chromatograph (GC) system capable of measuring concentrations of eight species of volatile organic compounds (VOCs) in a near-real-time fashion. Samples were taken at several points within the SCC, to generate species profiles with respect to system residence time. For the experiments, the afterburner on the SCC was operated at conditions ranging from fuel-rich to fuel-lean, while the kiln was operated at a constant set of conditions. Results indicate that combustion of  $\text{CH}_2\text{Cl}_2$  produces higher levels of measured PICs than combustion of  $\text{CCl}_4$ , particularly 1,2 dichlorobenzene, and to a lesser extent, monochlorobenzene. Benzene emissions were predominantly affected by the afterburner air/fuel ratio regardless of whether or not a surrogate waste was being fed.

## INTRODUCTION

The secondary combustion chamber (SCC) is an important piece of control equipment for rotary kiln incinerators.<sup>1,2</sup> The SCC should be capable of destroying any unburned

organic material that exits the primary combustion chamber due to rogue droplets, transients, quenching, or incomplete mixing. SCCs are also commonly used to combust liquid wastes that have high heating values. Design criteria in the past have been mostly limited to a time-temperature requirement, such as 2 sec at 1000 °C (1800 °F). Although a time-temperature requirement is not written into the hazardous waste incinerator regulations as defined in the Resource Conservation and Recovery Act (RCRA), it appears to have been adopted as a *de facto* criterion by regulators and the regulated community alike. A disadvantage of this "apparent" policy is that mixing, known to be of critical importance in incineration systems,<sup>3</sup> is largely ignored, and no economic incentives exist to improve afterburner designs, given that any new design would likely require a certain time-temperature profile before it could be installed, even if such a design could meet required emissions limits with a much more compact configuration.

The emissions that the SCC must deal with generally result from some sort of system failure in the primary chamber, since steady-state operation of the primary chamber generally eliminates the need for an SCC. Liquid injection incinerators, for example, typically do not require an SCC. The failure modes that can cause elevated levels of organic compounds to enter the SCC include mixing failures, such as those caused by poor microscale mixing intensities or poor macroscale mixing; poor atomization; flow stratification; batch charging and depletion of oxygen in the primary chamber; and reaction quenching, such as that caused by unburned material entering cold regions of the combustion device, or by cold walls. Rotary kilns in particular exhibit high levels of flow stratification,<sup>4-6</sup> and typically have some of their waste feed fed in batches and, as such, generally employ an SCC.

Part of the reason that a time-temperature requirement is used as a common SCC design criterion is that the effects of turbulence and complex chemical kinetics are not understood well enough to incorporate their use into the permitting process. It is very important, however, to work toward

## IMPLICATIONS

This study highlights ongoing research within EPA supporting development of hazardous waste incineration regulations. It shows the ability to measure in a near-real-time mode trace products of incomplete combustion directly from the combustion device, rather than using extractive sampling that takes weeks before results are available. In addition, this preliminary work attempts to correlate overall incinerator performance to the measured concentrations of certain volatile organic compounds. Future work should enable development of practical surrogate incinerator performance indicators to ensure minimum emissions of compounds of interest, e.g., dioxins.



gaining an understanding of kinetics and mixing in incinerators, since it is possible to have excessive levels of products of incomplete combustion (PICs) even after having successfully met the necessary time-temperature requirement. The EPA Air Pollution Prevention and Control Division, in cooperation with the New Jersey Institute of Technology (NJIT) and Massachusetts Institute of Technology (MIT), has been performing research on a pilot-scale rotary kiln incinerator simulator (RKIS) to complement laboratory-scale research being performed at both of the previously mentioned academic institutions, with the ultimate goal of furthering the state-of-the-art of SCC design by incorporating gas-phase mixing and kinetic considerations into the design criteria, particularly in regard to chlorocarbon combustion. Initial pilot-scale experiments have consisted of system characterization tests.

In order to incorporate gas-phase mixing and kinetic phenomena into afterburner design, it is necessary to achieve several goals, including:

- Development of reaction pathways and kinetic data for combustion of the principal organic hazardous constituents (POHCs) present in the waste, along with possible mechanisms of formation of PICs from POHC decomposition products. Although mechanistic information is not available for complex compounds, mechanisms do exist for  $C_1$  and  $C_2$  chlorocarbon combustion.<sup>7</sup> This paper focuses on combustion of carbon tetrachloride and methylene chloride, compounds for which kinetic mechanisms exist.
- Development of models that take into account macromixing and micromixing phenomena to aid in the scale-up of results from very small-scale experiments to pilot and full-scale systems. Kinetics and thermodynamics alone cannot account for emissions of PICs from incinerators. Mixing must eventually be considered.<sup>8</sup>
- Development of techniques to measure trace organic species or surrogates for trace organic species in the field, given that many of the advanced diagnostics available in a laboratory setting cannot easily be transferred to a field application. Semi-continuous measurement of key organic compounds can potentially be used to characterize the overall destruction of all hazardous trace organics of concern.

The NJIT and MIT groups have used small-scale reactors that can be operated under very controlled conditions to verify kinetic mechanisms.<sup>7,8</sup> However, once these mechanisms have been developed, a mixing model must be used to apply the kinetics to a practical system. This paper reports on the initial results from the pilot-scale testing program, where an on-line gas chromatograph (GC) has been developed for monitoring trace organic compounds of interest in a near-real-time fashion, and then used during

combustion tests burning carbon tetrachloride and methylene chloride to develop a database for use in future modeling work. Results from this study will be used to develop and refine SCC reactor models under development at NJIT.

## EXPERIMENTAL

### Rotary Kiln Incinerator Simulator

The EPA/APPD Rotary Kiln Incinerator Simulator (RKIS) is located in the EPA Environmental Research Center hazardous waste incineration research laboratory in Research Triangle Park, NC. The facility has a RCRA Research, Development, and Demonstration (RD&D) permit to burn actual and surrogate hazardous waste.

The 73 kW (250,000 Btu/hr) prototype rotary kiln thermal destruction unit was designed for the testing of liquid and solid surrogate hazardous waste materials and is shown in Figure 1. This facility has been described in detail elsewhere.<sup>9,10</sup> Note the locations of sampling points (numbers) and dopant injection points (letters) on the figure. The RKIS was designed to contain the salient features of full-scale kilns, but still be sufficiently versatile to allow parametric experimentation by varying one parameter at a time or controlling a set of parameters independently. The rotating kiln section contains a 0.610 m (24 inch) long, 0.763 m (30 inch) diameter recess which contains the solid waste during incineration. The recess was designed with a length-to-diameter (L/D) ratio of 0.8, which is 20% to 25% of a full-scale system.

The main burner (Eclipse 82 MVTA) is the primary heat source for the system. Natural gas is used as the primary fuel. The primary chamber (kiln section) rests on two trunion assemblies and is driven by a motor and gear drive. Consistent rotational speeds between 0.4 rpm and 4.5 rpm are possible. Seals between the kiln and the transition section

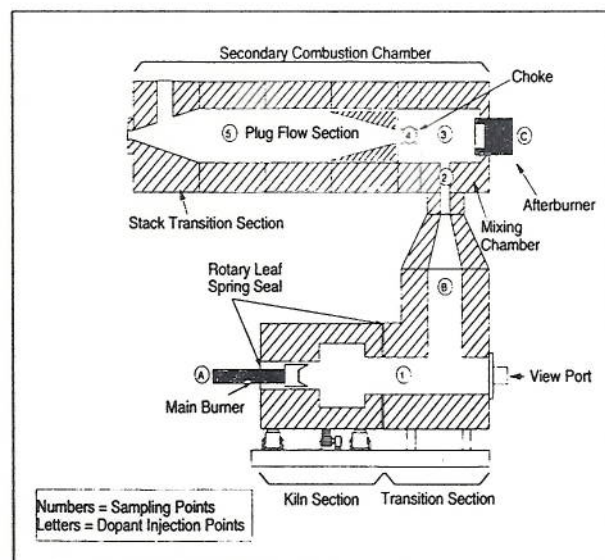


Figure 1. Rotary kiln incinerator simulator.



and main burner extension are made with Teflon gasketed rotary leaf springs. From the kiln section, the combustion gases enter the transition section.

The gases then flow into the experimental 73 kW (250,000 Btu/hr) SCC. The SCC consists of three regions: the 0.610 m (24 inch) diameter mixing chamber, the 0.610 m (24 inch) diameter plug flow section, and the stack transition section. A replaceable choke section separates the mixing chamber from the plug flow section. Currently, the installed choke has a 15.24 cm (6 inch) diameter. A conical refractory insert has been installed into the first plug flow sub-section to provide a gradual divergence from the choke diameter to the plug flow section diameter and minimize recirculation zones downstream of the choke. The afterburner (ACI Pyrotron) provides heat and flame to this SCC, and is capable of operating using air or oxygen-enriched air as the oxidizer. It is also possible to operate the SCC as an oxidizer injection device by allowing air flow through the burner with no natural gas. For these tests, air was the only oxidizer used.

Liquid surrogate waste was injected at point B (see Figure 1) using 652.9 kPa (80 psig) nitrogen ( $N_2$ ) and an air atomizing nozzle, as shown in Figure 2. The  $N_2$  pushes the liquid into the aspiration system, where it is atomized by 0.012  $m^3/min$  (25 scfh) of compressed air at 170.3 - 273.7 kPa (10-25 psig). A proportional solenoid control valve is used to control the flow rate of the selected organic liquid feed into the kiln. A rotameter is used to measure flow rates. The entire system is tied into the existing RKIS flame safety interlock system so that the waste feed is cut off if the RKIS main burner flame is extinguished. The system is equipped with a pressure release line so that when the pressure is released, vapors are vented into the RKIS and not into the laboratory. The two liquid surrogate wastes used in this study were carbon tetrachloride ( $CCl_4$ ) and methylene chloride (dichloromethane,  $CH_2Cl_2$ ).

The RKIS is equipped with a gas analysis and data acquisition system consisting of two sets of continuous emissions

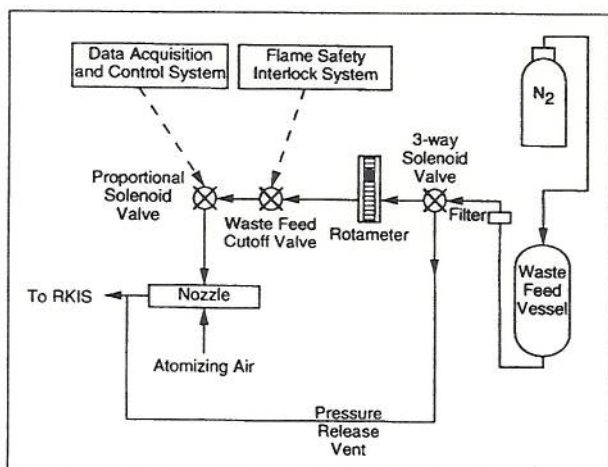


Figure 2. Liquid injection system.

monitors (CEMs) for oxygen ( $O_2$ ), carbon monoxide (CO), carbon dioxide ( $CO_2$ ), nitric oxide (NO), and total hydrocarbons (THCs), with sample locations at points 1 and 5 (see Figure 1). This setup allows simultaneous monitoring of gas-phase species at both the kiln exit and the SCC exit.

### On-Line Gas Chromatograph System

The RKIS is equipped with an on-line gas chromatograph (GC) system for measurement of trace volatile organic species. This GC adapts some of the methodologies used in the EPA standard Volatile Organics Sampling Train (VOST) method<sup>11,12</sup> to on-line use. Based on an initial screening test, the compounds listed in Table 1 were identified using reference samples and selected as target analytes. Other species of interest that were not anticipated in the original screening test, such as methylene chloride, were separately quantified later.

The on-line GC analytical system (Figure 3) contains a heated sample delivery system, a purge and trap sample concentrating system, and the GC analytical system. Samples were withdrawn using a non-cooled piece of 0.635 cm OD (0.25 in. OD) stainless steel tubing. The heated sample delivery system consists of a heated glass fiber filter (125 °C) and an unheated water impinger positioned on the vacuum side of a heated head (125 °C) diaphragm pump nominally delivering 25 L/min. The filter and impinger system are used to remove particulate matter and HCl from the sample stream prior to reaching the sample pump. The effluent of the pump is routed through a heated Teflon sample line (150 °C) to the purge and trap sample concentrating system. A back pressure regulator (BPR), at the exit of the sample line but before a totalizing flow meter, delivers the SCC sample to the sample concentrator at a constant pressure and flow rate.

The sample concentrating device is a Tekmar LSC-2000 thermal desorption unit that has been modified

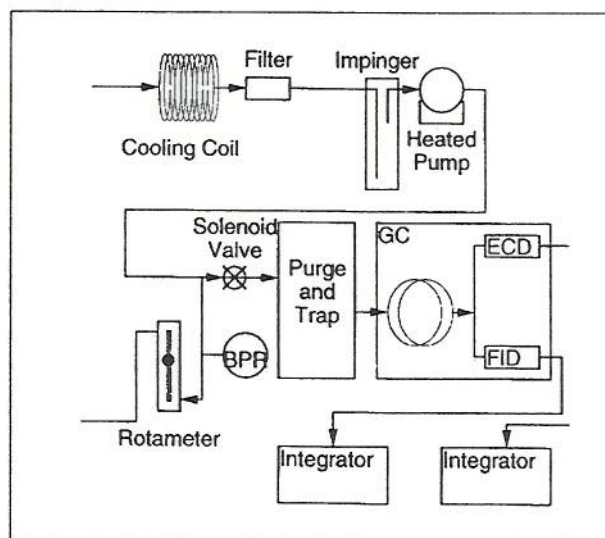


Figure 3. On-line GC system.



**Table 1.** List of target analytes for on-line GC system.

Compound	Formula	Detector	Det. Limit (ng on column)	Det. Limit Based on 200 ml Inj. ( $\mu\text{g}/\text{m}^3$ )
chloroform	$\text{CHCl}_3$	ECD	0.25	0.001
carbon tetrachloride	$\text{CCl}_4$	ECD	0.1	0.0007
benzene	$\text{C}_6\text{H}_6$	FID	1.0	0.005
toluene	$\text{C}_7\text{H}_8$	FID	1.0	0.005
trichloroethylene	$\text{C}_2\text{HCl}_3$	ECD	3.0	0.015
perchloroethylene	$\text{C}_2\text{Cl}_4$	ECD	0.1	0.001
monochlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	FID	1.0	0.005
1,2, dichlorobenzene	$\text{C}_6\text{H}_4\text{Cl}_2$	FID	2.0	0.010

to accommodate the collection of combustion samples directly. A series of two electrically activated, normally open solenoid valves are located upstream of the inlet to the concentrating sorbent trap. The sorbent trap is 0.049 cm (1/8 inch) OD x 30.48 cm (12 inch) stainless steel tubing packed with 7.6 cm Caropak B and 1.3 cm Carbosieve S III. In the normally open position, the valves route the helium carrier through the trap. When the solenoid valves are energized, SCC emissions are diverted to the inlet of the trap at a constant pressure and flow rate. Flow rate is monitored and measured by a gas rotameter at the exit of the sorbent trap. The total sample time and flow are used to determine total stack gas volume sampled. Total sample volumes are nominally 200  $\text{cm}^3$  to minimize the sample breakthrough volume of the lowest boiling point volatile organic compound (VOC) species of interest. Following sampling, the solenoid valves are returned to the normally open position, the trap ballistically heated to 250  $^{\circ}\text{C}$ , and the effluent diverted to the GC analytical system. The "Purge Ready" temperature of the concentrator was raised to 43  $^{\circ}\text{C}$  due to the high ambient temperatures in the laboratory. The adsorbent trap was quickly heated to 210  $^{\circ}\text{C}$  to efficiently transfer accumulated organic compounds through a heated transfer line (210  $^{\circ}\text{C}$ ) to a cryogenically cooled GC oven, set at 10  $^{\circ}\text{C}$ .

The GC analytical system is a HP 5890 series II GC equipped with both flame ionization (FI) and electron capture (EC) detectors. The VOCs collected and transferred to the GC are separated by a Rtx-624 0.53 mm ID x 75 m fused silica capillary column (Restek Corp., 3.0  $\mu\text{m}$  film thickness). The GC was temperature ramped to separate the accumulated organics into quantifiable, individual compounds. The temperature program used for the GC is: 10  $^{\circ}\text{C}$  hold 0.00 min.; ramp at 6  $^{\circ}\text{C}/\text{min}$  to 110  $^{\circ}\text{C}$ ; hold 2 min.; ramp at 10  $^{\circ}\text{C}/\text{min}$  to 200  $^{\circ}\text{C}$ ; hold 3 min. The carrier gas is 7.5 mL/min of  $\text{N}_2$ . The effluent of the column is split (ratio 9:1, respectively) to deliver sample to both the FID and ECD simultaneously. Electronic analog integrators relate integrated peak areas to sample concentration.

A single point calibration was used to quantify all organic compound amounts. It is realized that higher concentrations of individual compounds may suffer a greater

degree of error when compared to lesser amounts of the same compound. A series of tests was performed to assess total system integrity and bias. Known concentration VOCs were prepared in 80 L Tedlar bags and sampled through the entire sample delivery system. Greater than 50% recovery was observed for all analytes of interest.

## EXPERIMENTAL PROCEDURES

The experiments were designed to examine differences in SCC effectiveness under system failure mode conditions at three sample locations (residence times) within the SCC and at three operating conditions of the afterburner, as defined by the afterburner stoichiometric (air/fuel) ratio (SR). This particular set of experiments concentrated on the potential failure mode of poor atomization by varying the pressure of the atomizing air in the liquid waste feeder. After a series of experiments were performed using  $\text{CCl}_4$  as the surrogate waste dopant, it was suggested that the PICs may be different from burning  $\text{CH}_2\text{Cl}_2$  as the dopant. Since the ultimate goal of this research is to eventually model chlorocarbon combustion in the afterburner, compounds were chosen based on availability of mechanistic data.  $\text{CH}_2\text{Cl}_2$  was used principally because a developed and validated mechanism for  $\text{CH}_2\text{Cl}_2$  combustion was available, and it was felt that  $\text{CCl}_4$  results could not be directly applied to a  $\text{CH}_2\text{Cl}_2$  mechanism. Therefore several additional tests were run using  $\text{CH}_2\text{Cl}_2$  as the surrogate waste, although the  $\text{CH}_2\text{Cl}_2$  test matrix was not as complete as that of the  $\text{CCl}_4$ . In addition,  $\text{CH}_2\text{Cl}_2$  was added to the original list of target analytes and elution times, and response factors were determined. The test matrix is shown in Table 2.

The mean droplet size of the atomized spray needed to be altered in order to examine the effects of rogue droplets passing through the afterburner. However, when testing was initiated, the equipment was not available to directly measure the droplet size except for water, which would not give valid results that could be applied to  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$ . Therefore it was decided that the extremes of the operating range of the atomizer would be used as the two cases. In this test matrix, the high atomization pressure case was achieved by operating the atomizing air at 273.7 kPa (25 psig). The low



**Table 2.** Test matrix.

Sample Location/Atomization Pressure	3	4	5
High			
carbon tetrachloride	S	RL	RLS
methylene chloride	S	RL	RL
Low			
carbon tetrachloride	S	RL	RLS
methylene chloride	-	-	-
Blank	S	RL	RLS

S - afterburner operated at SR=1

R - afterburner operated fuel rich, SR=0.85

L - afterburner operated fuel lean, SR=1.1

atomization pressure case was achieved by operating the atomizing air at 170.3 kPa (10 psig), which was as low as the pressure could be set while still maintaining 0.012 m<sup>3</sup>/min (25 scfh) of atomizing air flow. The 0.012 m<sup>3</sup>/min (25 scfh) is the recommended air flow for the nozzle. An increase or decrease in air flow could have been used to attempt to vary atomization; however, this would have influenced the local air/waste ratio near the injector and

would likely confound the data. Ultimately, though, the droplet size distribution was measured, and no significant difference was found between the droplet size distribution at the two atomization pressures used. Therefore the high and low pressure cases can be assumed to be identical for statistical purposes.

Throughout all of the tests, the primary natural gas burner was operated at a constant 73 kW (250,000 Btu/hr) firing rate at near-stoichiometric conditions, and the afterburner was operated at a constant 51 kW (175,000 Btu/hr), resulting in temperatures of approximately 1000 °C (1832 °F) throughout the system. The kiln needed to be operated on low excess air so that significant combustion would not occur in the transition duct due to excess oxygen from the kiln effluent. The gases leaving the kiln had an oxygen concentration of 1 % by volume, which varied slightly due to air in-leakage and cycling of the induced draft air control system. The combustion conditions in the SCC were changed by varying the combustion air entering the afterburner. In the tests, the liquid injection device was filled with approximately 500 mL of CCl<sub>4</sub> or CH<sub>2</sub>Cl<sub>2</sub> in a nearby fume hood, and installed on the feeder. The feeder was activated and

**Table 3.** Test conditions and emissions results.

Run	Dopant	AB SR	Port	Res. Time(s)	CH <sub>2</sub> Cl <sub>2</sub> (mg/m <sup>3</sup> )	CHCl <sub>3</sub> (mg/m <sup>3</sup> )	CCl <sub>4</sub> (mg/m <sup>3</sup> )	Benzene (mg/m <sup>3</sup> )	Toluene (mg/m <sup>3</sup> )	TCE* (mg/m <sup>3</sup> )	PERC** (mg/m <sup>3</sup> )	CB*** (mg/m <sup>3</sup> )	DCB**** (mg/m <sup>3</sup> )	Stack Flow (Nm <sup>3</sup> /min)	DE (%)	TOTAL (mg/m <sup>3</sup> )
0622RG4	CCl <sub>4</sub>	0.85	4	3.445	1.747	0.016	0.012	14.735	3.301	0.273	0.287	2.582	0.000	2.27	>99.9999	22.953
0616RP5	CCl <sub>4</sub>	0.85	5	4.714	0.427	0.005	0.349	10.770	0.761	0.049	0.009	2.264	0.000	2.27	99.9994	14.634
0615RG5	CCl <sub>4</sub>	0.85	5	4.714	0.240	0.006	0.585	11.025	0.317	0.078	0.002	1.059	0.000	2.27	99.9989	13.312
0621SP3	CCl <sub>4</sub>	1	3	1.9174	0.313	0.187	0.136	0.036	0.028	0.099	0.026	0.020	0.000	1.56	99.9998	0.845
0621SG3	CCl <sub>4</sub>	1	3	1.9174	0.000	0.082	0.149	0.031	0.045	0.098	0.027	0.082	0.000	1.56	99.9998	0.514
0614SG5	CCl <sub>4</sub>	1	5	4.714	0.083	0.012	0.268	0.009	0.011	0.044	0.033	0.061	0.000	2.38	99.9995	0.521
0615SP5	CCl <sub>4</sub>	1	5	4.714	0.000	0.007	0.311	0.009	0.019	0.080	0.003	0.054	0.000	2.38	99.9994	0.483
0622LG4	CCl <sub>4</sub>	1.1	4	3.445	0.439	0.115	0.078	1.165	0.064	0.124	0.159	0.096	0.000	2.50	99.9998	2.24
0620LG5	CCl <sub>4</sub>	1.1	5	4.714	0.000	0.004	0.111	0.018	0.010	0.059	0.001	0.006	0.000	2.50	99.9998	0.209
0616LG5	CCl <sub>4</sub>	1.1	5	4.714	0.000	0.004	0.221	0.046	0.061	0.068	0.004	0.255	0.000	2.50	99.9996	0.659
0620LP5	CCl <sub>4</sub>	1.1	5	4.714	0.000	0.006	0.088	0.026	0.008	0.048	0.001	0.012	0.000	2.50	99.9998	0.189
0623MRG4	CH <sub>2</sub> Cl <sub>2</sub>	0.85	4	3.445	3.200	0.032	0.005	9.946	1.752	0.260	0.221	16.571	8.087	2.27	99.9932	40.074
0623MRG5	CH <sub>2</sub> Cl <sub>2</sub>	0.85	5	4.714	0.931	0.003	0.002	8.806	0.289	0.122	0.021	2.165	0.270	2.27	99.9980	12.609
0621MSG3	CH <sub>2</sub> Cl <sub>2</sub>	1	3	1.9174	2.109	0.207	0.020	5.640	0.185	0.127	0.071	19.917	0.422	1.56	99.9969	28.698
0623MLG4	CH <sub>2</sub> Cl <sub>2</sub>	1.1	4	3.445	0.398	0.066	0.040	0.306	0.014	0.097	0.060	0.018	0.000	2.50	99.9991	0.999
0623MLG5	CH <sub>2</sub> Cl <sub>2</sub>	1.1	5	4.714	0.411	0.063	0.005	0.609	0.043	0.091	0.010	0.289	0.297	2.50	99.9990	1.818
0622RB4	n/a	0.85	4	3.445	0.000	0.000	0.001	9.376	2.666	0.029	0.001	0.017	0.000	2.27	n/a	12.09
0615RB5	n/a	0.85	5	4.714	0.000	0.000	0.135	12.340	0.426	0.075	0.002	0.019	0.000	2.27	n/a	12.997
0620RB5	n/a	0.85	5	4.714	0.000	0.000	0.001	10.482	0.328	0.037	0.001	0.000	0.000	2.27	n/a	10.849
0621SB3	n/a	1	3	1.9174	0.000	0.002	0.002	0.062	0.022	0.048	0.002	0.037	0.000	1.56	n/a	0.175
0621SB3	n/a	1	3	1.9174	0.069	0.006	0.001	0.203	0.028	0.057	0.002	0.760	0.272	1.56	n/a	1.396
0620SB5	n/a	1	5	4.714	0.000	0.000	0.001	0.263	0.009	0.054	0.001	0.000	0.000	2.38	n/a	0.326
0615SB5	n/a	1	5	4.714	0.000	0.000	0.000	0.007	0.012	0.052	0.002	0.059	0.000	2.38	n/a	0.132
0614SB5	n/a	1	5	4.714	0.000	0.000	0.000	0.005	0.009	0.045	0.000	0.000	0.000	2.38	n/a	0.059
0622LB4	n/a	1.1	4	3.445	0.000	0.003	0.001	0.306	0.015	0.013	0.006	0.009	0.000	2.50	n/a	0.353
0620LB5	n/a	1.1	5	4.714	0.000	0.000	0.002	0.006	0.007	0.080	0.002	0.013	0.000	2.50	n/a	0.11
0616LB5	n/a	1.1	5	4.714	0.000	0.000	0.022	0.567	0.032	0.075	0.002	0.102	0.000	2.50	n/a	0.8

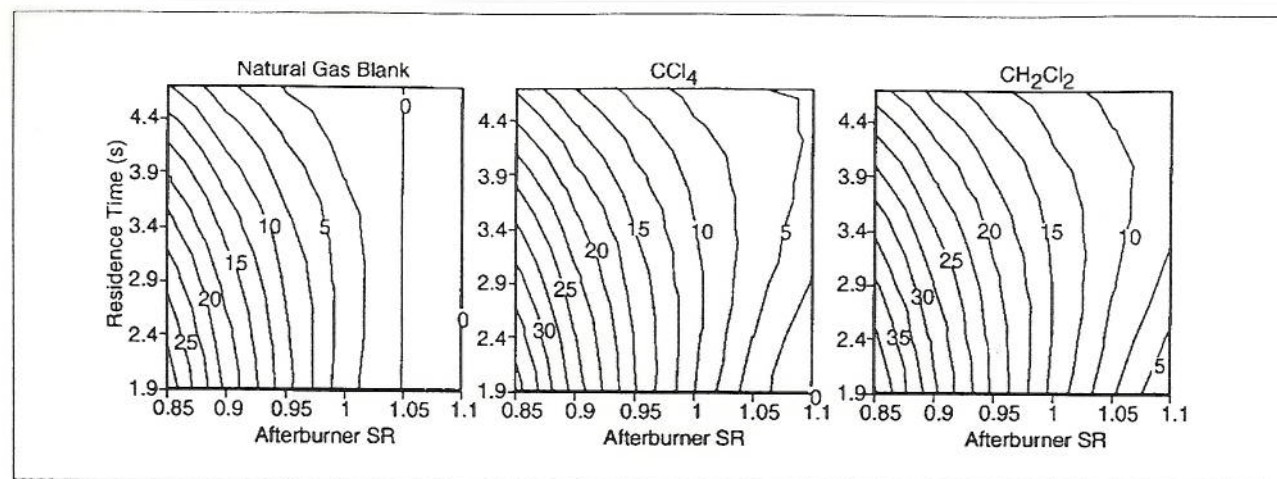
\* - trichloroethylene

\*\* - perchloroethylene

\*\*\* - monochlorobenzene

\*\*\*\* - 1,2, dichlorobenzene





**Figure 4.** Linear regression analysis results of total identified PIC emissions versus afterburner stoichiometric ratio and residence time.

ran for 30 sec at a feed rate of 80 mL/min to allow the system to stabilize, injecting the dopant at point B (see Figure 1). At that time, the GC sample valve was activated, and a sample was pulled from the afterburner (at point 3, 4, or 5 as per Figure 1) for 5 minutes, while the run conditions were held in steady-state. The purge and trap cycle was then initiated and finally the chromatography was completed. In all, each run took approximately 40 minutes from start to finish. The chromatograms were then analyzed and concentrations were calculated based on response factors derived from calibration standards.

## RESULTS

The test conditions and results are shown in Table 3. The mean residence times reported in Table 3 were derived from sulfur dioxide ( $\text{SO}_2$ ) tracer studies,<sup>13</sup> and represent the mean residence time between the injector at point B and the sample point (3, 4, or 5). The complete results of the tracer studies will be reported elsewhere in greater detail. We observed that some of the blanks, particularly those taken after chlorinated species were run through the RKIS, resulted in low but measurable concentrations of some chlorinated species. This anomaly was traced and is probably due to some residual material remaining in the impinger water and/or sorbent trap. Future studies will attempt to establish criteria for cleaning the purge and trap system in between runs to minimize possible cross-contamination. In addition, trichloroethylene (TCE) was found as a contaminant in the blanks, and was detected in all samples. Although some of the samples exhibited elevated levels of TCE, which likely was generated as a PIC, the level of the TCE contaminant in the GC system made it difficult to attribute all but the highest levels of TCE (found in the samples taken at sample port 4) as being outside the contaminant levels. In addition, we believe that the  $\text{CCl}_4$  data from the sample at port 4 during the fuel-rich case was obscured by a spurious peak and was reported to be 0.012 mg/m<sup>3</sup>, which is lower than every other

$\text{CCl}_4$  run, and we believe this to be an outlier. This condition will be re-run in the future.

No statistical significance was noted between the results for the high and low atomizing pressure cases. Future experiments will necessitate changing the nozzle on the atomizer in order to vary droplet size. Equipment is being designed to directly measure the droplet sizes in the sprays while the surrogate wastes are being fed, using an enclosed spray simulator in a laboratory fume hood.

In general, combustion of  $\text{CH}_2\text{Cl}_2$  produced much higher quantities of identified PICs than combustion of  $\text{CCl}_4$ , particularly during fuel-lean combustion, which is the desired operating mode for incinerators. This observation has implications with regards to RCRA trial burns. According to the incinerability index developed by Dellinger,<sup>14,15</sup> the fully halogenated  $\text{CCl}_4$  is more difficult to destroy than the partially halogenated  $\text{CH}_2\text{Cl}_2$ . Past studies of incineration of chlorofluorocarbons (CFCs) also show that the fully halogenated CFCs produce very low PIC emissions.<sup>16,17</sup>  $\text{CCl}_4$  is commonly used during RCRA trial burns as a POHC<sup>18</sup> since it is not believed to be a common PIC from incomplete combustion of chloroorganics (note in Table 3, though, that  $\text{CCl}_4$  was measured as a PIC from  $\text{CH}_2\text{Cl}_2$  combustion). Although  $\text{CCl}_4$  may be useful as a POHC due to its high thermal stability, and provide a useful measure of a system's ability to meet the required 99.99 % destruction and removal efficiency (DRE), it may not challenge an incinerator's propensity to create or ability to destroy PICs. Keep in mind, though, that these experiments were performed using only  $\text{CCl}_4$  or  $\text{CH}_2\text{Cl}_2$  as the principal feeds, rather than the complex mixtures used during trial burns. Figure 4 shows the results of a linear regression analysis of the data, illustrating the totals of all identified PICs from Table 3 correlated versus residence time and afterburner SR.

Figure 5 illustrates the emissions of benzene from all of the runs, including the blanks. The afterburner SR appears to be the critical factor in determining emissions of



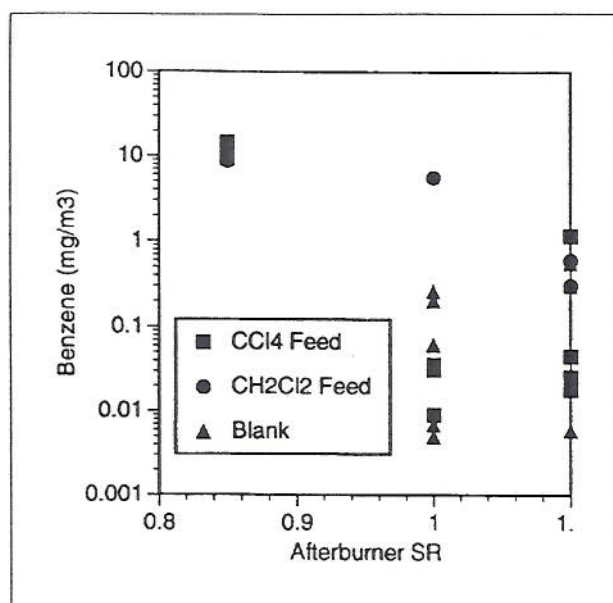


Figure 5. Benzene versus afterburner stoichiometric ratio.

benzene. Interestingly, emissions of benzene during the fuel-rich case were not significantly different from those found in the natural gas blanks, indicating that the natural gas contributed most of the benzene in the fuel-rich samples. However, note that in the fuel-lean cases, emissions of benzene from the  $\text{CCl}_4$  burns are of the same order of magnitude as the blanks. During  $\text{CH}_2\text{Cl}_2$  combustion, benzene emissions appear to be slightly higher than those found in the blanks and the  $\text{CCl}_4$  tests, although more testing will be necessary to determine whether the difference is statistically significant. This phenomenon is consistent with the findings of Dellinger<sup>13,14</sup> that ring structures were not predominant PICs from thermal decomposition of  $\text{CCl}_4$ .

A significant difference between the  $\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2$  runs can be found by examining the data for monochlorobenzene and 1,2 dichlorobenzene. Emissions of monochlorobenzene were higher during  $\text{CH}_2\text{Cl}_2$  runs, particularly during the fuel-rich conditions and during the short residence time run. It appears that significant amounts of monochlorobenzene were produced from incomplete combustion of the  $\text{CH}_2\text{Cl}_2$ , but were not produced in significant quantities from the  $\text{CCl}_4$  tests. Differences in the emissions of 1,2 dichlorobenzene are even more pronounced than with the monochlorobenzene. With the exception of one of the blank samples (which is an apparent cross-contaminant), 1,2 dichlorobenzene was measured only during runs burning  $\text{CH}_2\text{Cl}_2$ . Since combustion of  $\text{CH}_2\text{Cl}_2$  resulted in levels of benzene comparable to those found in the natural gas blanks, and levels of monochlorobenzene and 1,2 dichlorobenzene were much higher than those found from  $\text{CCl}_4$  combustion, it may be possible that  $\text{CH}_2\text{Cl}_2$  can readily form chlorinated intermediate structures (possibly acetylenes or chlorinated acetylenes) that are ring-growth precursors,

resulting in direct formation of monochlorobenzene and dichlorobenzene rather than from chlorination of benzene. Note, however, that only the ortho-substituted dichlorobenzene was measured. It may be that meta- or para-substituted dichlorobenzenes were formed from  $\text{CCl}_4$  combustion. Future investigation into these potential ring growth precursors may show them to be potential surrogate performance indicators to ensure good combustion in the incinerator. Since chlorobenzenes have been implicated as precursors to polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/PCDF) formation, it would make sense that measurement of the precursor to chlorobenzenes could be a useful indirect indicator of the potential for formation of PCDD/PCDF, and that control of this precursor could inhibit formation of PCDD/PCDF.

## CONCLUSIONS

Although a few problems exist with the current on-line GC setup, as with most prototype measurement instrumentation, it was highly successful at measuring several chlorinated and non-chlorinated PICs with an approximately 40-minute turnaround time. Detection levels were sufficient to quantify  $\text{CCl}_4$  and  $\text{CH}_2\text{Cl}_2$  destruction efficiencies in excess of 99.999%, as well as being able to quantify several common PICs down to the low parts per billion level. The system was able to quantify emissions of benzene and toluene from a natural gas combustion blank. TCE was found as a contaminant in all samples, and its source is being sought. Cross-contamination between back-to-back samples also appears to be a minor problem, and future work may establish procedures to minimize cross contamination.

Combustion of  $\text{CH}_2\text{Cl}_2$  results in levels of 1,2 dichlorobenzene and monochlorobenzene much higher than those found from  $\text{CCl}_4$  combustion. It may be possible that  $\text{CH}_2\text{Cl}_2$  can readily form chlorinated intermediate structures that are ring-growth precursors, resulting in direct formation of monochlorobenzene rather than from chlorination of benzene. Future work may involve measurement of 1,3 and 1,4 substituted dichlorobenzene as well.

Combustion of  $\text{CH}_2\text{Cl}_2$  produced higher quantities of identified PICs than combustion of  $\text{CCl}_4$ , particularly during fuel-lean combustion. Although  $\text{CCl}_4$  may be useful as a POHC due to its high thermal stability, and provide a useful measure of a system's ability to meet the required 99.99% DRE, it may not challenge an incinerator's ability to produce or destroy PICs.

Areas of the on-line GC system requiring further work include:

- Elimination of TCE as a contaminant
- Development of procedures to minimize cross-contamination of samples in series
- Comparison of results to EPA standard methods
- Expansion of target analyte list



Areas of the SCC requiring work include:

- Investigation into potential ring-growth precursors for use as surrogate performance indicators
- Achieving better simulation of rogue droplet formation and variable droplet size for experiments
- Testing a wider variety of waste dopants, including chloroform
- Using kinetic models of C<sub>1</sub> and C<sub>2</sub> chlorocarbon combustion to compare with experimental results

## ACKNOWLEDGMENTS

The authors would like to thank John Dawkins (an EPA Senior Environmental Employee) who operated the CEM systems for the RKIS, Mark Calvi of Acurex Environmental, who operated the FGCS system, and Bill Preston of Acurex Environmental, who set up and operated the on-line GC system. Portions of this work were performed under EPA Contract 68-D4-0005 with Acurex Environmental.

## DISCLAIMER

The research described in this article has been reviewed by the Air Pollution Prevention and Control Division, U.S. Environmental Protection Agency, and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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